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(71) Applicant *(for all designated States except US)*: PETRAMEC, INC. [US/US]; Ben Franklin Technology Center, 115 Research Drive, Jordan Hall, Bethlehem, PA 18015 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: BIELSKI, Roman [PL/US]; 1308 Sheridan Road, Coopersburg, PA 18036 (US). CARTER, John, E. [GB/US]; 411 Trails Court, Houston, TX 77024 (US).

(74) Agent: COOK, Tim; Felsman, Bradley, Vaden, Gunter & Dillon, LLP, One Riverway, Suite 1100, Houston, TX 77056 (US).

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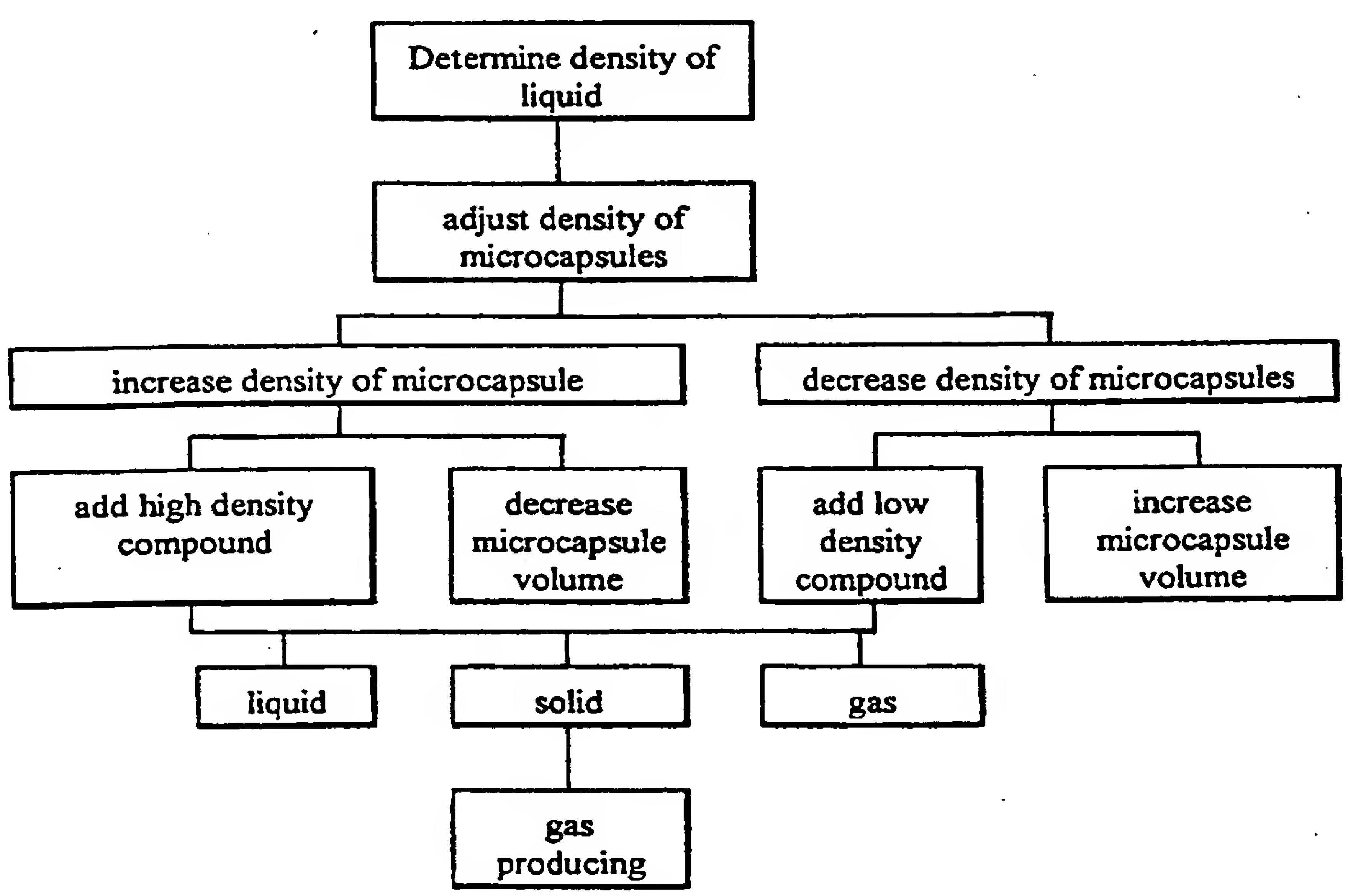

(57) Abstract

A method of making a liquid having a substantially uniform distribution of microcapsules having their density adjusted to approximate the density of a liquid. The microcapsules may be structured to encapsulate a payload including an additive that may be released upon a triggering condition as a marker which may be detected either externally or by internal. A method is taught that may be used to calculate the volume of a tank.

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METHODS OF MAKING AND USING MICROCAPSULES WITH CONTROLLED DENSITY

Field of Invention

This invention relates to a method of making and using microcapsules with controlled density, and more particularly, using said microcapsules for uniformly distributing additives and markers in a liquid.

Background of the Invention

Microencapsulation may be described as the formation of a polymeric matrix or shell around the droplets or particles of given core substance". Usually, it is employed to prevent contact between the selected (core) material and the environment. It has been successfully applied to solving multiplicity of problems for more than forty years. Microencapsulation was found in numerous agriculture, biomedical, consumer product and industrial applications. Moreover, microencapsulation is found in foods, cosmetics, printing, agricultural products and detergents. The purpose of microencapsulation can be many-sided. Various chemicals have been microencapsulated to prevent their evaporation (for volatile chemicals), to minimized their contact with the users (for toxic or dirtying substances), to promote the ease of handling of the core material, to mask the taste of the core or to prevent undesired reactions. it must be pointed out that, practically. all the prior art applications of microencapsulation are related to solid capsules or to a slurry of capsules in a liquid. Recently, an exploding interest can be observed in research and applications related to controlled release of drugs. A number of the publications in the "Journal of Microencapsulation" have been devoted to this subject. In this case the liquid medium is very specific (body fluid) and the microencapsules are not uniformly spread throughout the liquid system.

The use of microcapsules in liquid media is possible. However, it has been applied only to mixtures which are not pumped over long distances and the core substance did not have to be uniformly distributed in the medium. The idea

of a liquid with uniformly distributed microcapsules is very attractive. A few features of such liquid systems are of major importance.

As is general for microcapsules, if not released, the encapsulated core substance is not substantially in contact with the environment (liquid medium).

The capsules may be separated from the liquid by filtration and measured or reused.

The core substance (payload) may be released into the liquid either in the controlled (slow) manner or "on command" (rapid release).

Most liquid compounds we encounter in everyday life contain some additives. They serve various purposes. In case of drinkable or edible products for human or animal consumption, they can fulfill highly diverse functions such as prevention of the growth of microorganisms, prevention of oxidative reactions (antioxidants), requirements or dietary regulations (calcium compounds in milk or juice) etc. Non-edible or drinkable products almost always contain some additives, also. For example, fuel additives can act as corrosion inhibitors, pour point depressants, emulsifying agents, can control combustion chamber deposits and so on.

It would be very advantageous to hinder the contact between dissolved components or between a component and the solvent, i.e., between different additives or additive and the main component of the liquid phase. For example, it is becoming more and more common to mark various liquid products to prove the point of origin or to prevent theft. In the case of drinkable or edible products, there is always certain concern that the added label may not be absolutely safe for consumption. Physical removal of an additive or a label before selling the product would eliminate these concerns. In case of such liquid products as fuels, there is always a concern that potential markers may react with fuel components or may be absorbed on the surface of such materials as pipes, pumps, tanks, that the marker may be in contact with. Some component of fuel additives are known to lose their activity due to undesired side reactions with other additives or markets.

Microencapsulation is the coating of small solid particles, liquid droplets, or gas bubbles with a thin film of coating or shell material. The size range of microcapsules is between 1 and 1000 microns (1mm = 1000micron). Most applications utilize microcapsules with diameter between 5 and 25 microns. Microencapsulation is performed for a variety of reasons. They include:

prevention of contact between the core (payload, encapsulate, the microcapsule content) and the environment until the selected time when the core is released, reduction of volatility or inflammability of liquids, enforcement of the size of droplets or particles of the core material, conversion of a liquid into a solid for easy and safe handling, prevention of the microencapsulated compounds from dissolving in other liquids such as water, and prevention of the core from coloring or dirtying the solution.

Microencapsulation was discovered in the forties, and introduced into practice in the fifties. The major application of microencapsulation is in the production of carbonless copy paper which today is a well in excess of $5 billion dollar business. Also, microencapsulated products in use include food ingredients, pesticides, fragrances and other cosmetics components, enzymes in the washing powder, flame retardants et cetera. Furthermore, the controlled release of drugs into the blood or gastrointestinal system is a very fast growing area of research and applications of microencapsulation.

Today, there are dozens of methods for making microcapsules, dozens of polymers that can form the wall (shell) material and there are several mechanisms of releasing the core material. The most common release is "controlled release" which usually relates to a slow release wherein the rate of release is as constant as possible. The controlled release can be caused by various processes. The most common approach takes advantage of diffusion of the core material through the permeable wall. Presently there is much less data pertaining to "on command" (rapid) release. The "on command" release can be caused by various stimuli such as:

pH or ionic strength change, osmotic or mechanical pressure increase, ultraviolet (UV), visible light, electron or laser beam, ultrasound, temperature increase, and appropriate enzymes.

These applications require the ability to produce microcapsules with relatively small, uniform diameter and well defined density. Additionally, the wall material must be capable of releasing the core substance in a controlled way, "on command" or as a response to certain condition in the liquid. Moreover, since countless compounds can be encapsulated in liquids exhibiting diverse properties, the ability to response to various stimuli is essential. We have devised several methods of increasing or decreasing density of microcapsules via introduction into capsules substances of high or low density, addition of gases during microcapsules formation and use of polymers or other chemicals which produce gas under certain conditions. We are aware of no successful attempts to produce capsules with the density equal to the density of the liquid the capsules are in.

Perhaps the most economically interesting applications of this invention are related to petroleum products. A very small number of prior art microencapsulation applications relate to hydrocarbon mixtures. Specifically, there have not been microencapsulations performed on a large scale application in the petroleum industry since such scaling up has never been necessary. Moreover, the potential users of encapsulated oil taggants insist that usually the measurement should take place at the field. It is believed that such large scale applications are achievable, however no experience exists on rapid release of microencapsulated taggants.

If successful, the microencapsulation of additives introduced to liquids may have very significant impact on some industries. For example, new additives can be used. They have not been used before due to concerns that they may react with the liquid, other additives or tanks, containers or pipelines components. Microencapsulation prevents this. Also, some additives are used in amounts bigger than necessary to counteract the losses caused by some undesirable interactions. Microencapsulation may save on lost materials. Moreover,

microencapsulations can be separated from the original liquid. Thus, in the case of labeling, the separation may be equivalent to pre-concentration and significantly improve sensitivity of the used detection method.

The fuels used in cars, trucks, planes, power plants, and heaters are treated with plurality of so called "additives." These additives fulfill a variety of functions such as inhibiting corrosion, controlling or removing carbon deposits in the combustion chamber, lowering the point at which the fuel is still a liquid, improving pouring properties, acting as antioxidants and complexing agents et cetera. However, some of these additives are not compatible. Nevertheless, they frequently end up in the same mixture. Usually, several parties inject additives at various stages, but they are not necessarily aware what the other parties introduced. The problem is well known, but not loudly heralded by the industry. Moreover, some additives can adversely react with fuel components or pipelines and tanks. Some additives are volatile and water soluble, causing losses and tremendous environmental problems (for example, MTBE). Due to this incompatibility of some additives, their activity or concentration declines substantially with time.

The natural solution to all these problems is microencapsulation. The contact of these trouble-causing additives with their environment may be prevented by microencapsulating them in such a way that such additives will be released only when needed. This concept has several additional advantages. The additives of interest become a quasi-powder when microencapsulated, and thus, are much easier to introduce into the liquid fuel. The transportation of microencapsulated additives becomes much safer - potential spills pose less danger of poisoning, causing a fire and are easier to deal with.

The successful application of microencapsulation of certain additives requires that a major obstacle, uniform distribution of microcapsules, can be overcome. Presently, the additives are dissolved in the liquid fuel. It is a natural characteristic of solutions that components are uniformly distributed. Thus, any sample of the solution contains exactly the same percentage of each component. Typical microcapsules will either float at the surface of the solution or end up at

the bottom depending on the relative density of the capsules and the liquid they are in. It is desirable for uniform distribution of non-miscible particles in a liquid is that their density is approximate to the density of the liquid they are in (constant stirring or taking advantage of the Brownian motion is impractical).

Thus, one way to keep microencapsulated additives uniformly distributed in the fuel is to adjust the density of the microcapsules to make it approximately equal to the density of the fuel. Usually, this means that the density of the microcapsules must be lowered. However, in some cases such as MTBE, the density of microcapsules must be increased.

There is one more issue that has to be addressed before microencapsulation of fuel additives is executed: the release mechanism. There are four types of additives:

1. Additives that do not degrade in fuels. There is no point in microencapsulating them.

2. Additives that would degrade in fuels or cause degradation of other components.

For this very reason they have never been introduced to the industry practice. An active search for such chemicals is on-going. There is certain probability that water may be such a compound.

3. Additives that decompose in the fuel and that enhance fuel performance during or after combustion. These compounds should stay microencapsulated until the fuel approaches the engine. Then, the natural stimulus one can take advantage of is the temperature increase.

4. Additives that deteriorate, or cause deterioration but are intended to act at some point between the refinery and the engine (or the combustion chamber). These additives should be present in the fuel but at much lower levels than present. Such additives may be microencapsulated with slow release of the additive to ensure that their concentration stays always above certain level.

There is a growing trend toward introducing markers to various liquid products for the following purposes: Detection of illegal addition of other liquids (of lower quality). Proving, or what is often more important, disproving, the

origin of a spill. Tracking illegal activities related to the diluting of some products. Also, tracking illegal activities related to not adding required additives or adding smaller than necessary amounts.

Sometimes, the qualitative answers (the origin of illegal material) are satisfactory; sometimes accurate quantitation is needed. The market for tagging petroleum products began to grow in the early nineties, however, as the oil price declined this trend stopped. Fortunately this was only a temporary phenomenon and the marking of fuels has started to grow again.

All of the current technology markers suffer from a serious drawback. Due to the complexity of the petroleum liquids, the added components, and the variety of the conditions they can be in, it is possible for potential taggants to react with mixture components, and thus, affect the results of measurements. We are testing the feasibility of using microencapsulated dyes as taggants. Since, any quantitation requires that the dye is uniformly distributed in the petroleum product, the microcapsules must exhibit specific density. Additionally, the option of using very small microcapsules and taking advantage of Brownian motion is also of interest.

At this point, we believe that microcapsules with a dye as the core material may be used to quantitate via counting. Due to the presence of a specific dye inside the microcapsules and well defined diameter of these microcapsules, an appropriate instrument can distinguish marking microcapsules from other particles present in the liquid. Thus, the instrument capable of counting specific microcapsules would yield very accurate quantitation.

It is essential that other methods can be used to prove the correctness of the measurement. This can be achieved via rupture (mechanical force) of the microcapsules in collected aliquot followed by measurement of the color intensity.

We think that many of the problems, the use of additives is related with, can be eliminated when proper microencapsulation is used. Additives can be added to the liquid in microencapsulated form. Then, when needed, they can be removed from the mixture using filtration. Alternatively, they can release the

core substance into the solution. The release can be controlled (slow) or "on command". This approach enables also measurement of the added label if needed. In such a case the capsules, separated by liquid, are treated with appropriate stimulus the polymer is sensitive to (such as high temperature, UV or laser beam, ultrasound). It induces the microcapsules rupture and enables the measurement of the amount of label present inside the microcapsules.

We are aware of no attempts to produce microencapsulated additives for liquids that are introduced and transported in the liquid. There are few reasons for this. We believe that probably the need for such applications was not that acute. Also, new, "intelligent" polymers, responding with large property changes to small physical or chemical stimuli, became available recently. It must be pointed out that more and more additives, fulfilling plurality of functions, are added to various liquids. Microencapsulation of some of these additives is perhaps the only way to prevent contact between these additives in solution.

Some fuel additives are expected to act when in the engine. However, they cannot be introduced to the engine independently from the fuel. Thus, they are in contact with the fuel components for prolonged periods of time. During this time they react with additives or with delivery system components such as steel or polymers of tanks or pipelines. Due to resulting deterioration of additives, significantly bigger than necessary amounts have to be used. We propose to microencapsulate additives using temperature sensitive polymers. Next, when approaching the engine, the capsules are ruptured due to rising temperature. Thus, the additives are delivered to the point of interest, when they can perform the expected job, i.e., prevent or control formation of the carbon deposits.

Another group of fuel additives such as corrosion inhibitors or viscosity improvers act before the fuel reaches the step of combustion in the engine. Many of these additives deteriorate due to reactions with fuel or additives components. Again, microencapsulation using controlled release system can significantly decrease the necessary amounts of these additives compounds by keeping the concentration of released core substance at lower levels.

The necessary condition for successful application of most microencapsulations into liquids system is that the microcapsules are distributed uniformly in the liquid. This is not a trivial problem. It can be achieved if the density of microcapsules is the same as the density of the liquid. Although, it is very unlikely that the microcapsules average density is equal to the natural density of the liquid. Moreover, it would be a miracle if the temperature change of both densities was the same. Not all, but many liquids of interest such as gasoline and kerosene are used at varying temperatures.

Anyway, if successful, the ability to uniformly disperse microcapsules with the different additives throughout selected liquid, i.e., ability to control the microcapsules density can revolutionize some industries. It is of particular importance for liquids that are pumped or transported for long distances. Here are some potential applications: Microencapsulation of taggants in petroleum products, crude oil, or fuel additives. Microencapsulation of taggants of expensive liquid materials such as alcoholic beverages or perfumes. Microencapsulation of volatile and unhealthy components of a liquid mixture. For example, microencapsulation of such oxygenates as MTBE (methyl-tert-butyl ether) may be highly beneficial. MTBE is used to improve the octane number of the fuel and to decrease carbon monoxide emissions. It is highly volatile and much better soluble in water than "normal" components of gasoline. It is suspected as responsible for significant increase in occurrence of allergies including asthma in cities where substantial quantities of MTBE or similar compounds are added to gasolines. Also, it has been found in water reservoirs as a result of fuel leaking from underground tanks.

Microencapsulation of unpleasant or smelly components of the drinkable products (for example, microencapsulation of fish oil added to milk or orange juice). If the active (microencapsulated) component is uniformly spread throughout the liquid, the delivered amount is precisely proportional to the amount of administered liquid. The release mechanism should be related to low pH in the stomach.

Microencapsulation of flame retardants added to flammable liquids that are transported using pipelines or tank-cars. When the flammable material catches fire, the capsules are ruptured due to increased temperature and appropriate material is released. However, if the flame retardant was not released the capsules can be filtered off and reused. It enables employment of even expensive core materials.

Microencapsulation of volatile components of perfumes; the capsules rupturing on contact with the skin (body temperature) or in the presence of visible light after it is removed from the black container. Microencapsulation of active components of ear, nose, or eye drops (released at body temperature).

Microencapsulation of chemicals that can pasteurize the drinkable liquid; the release of the core should be triggered by the presence of microorganisms of interest. For example, the capsule wall can be made of the appropriate material (polysaccharides, proteins) digested by microorganisms. Unused capsules can be separated and reused.

Microencapsulation of easy oxidizable vitamins (such as vitamin A or E), nutrients (cod liver oil) or other food additives; of course, it makes sense only when these additives are introduced to the drinkable liquid product.

Microencapsulation of radioactive substances that can serve various purposes. After introduction of microencapsulated radioactive compound, one can take advantage of it, as the radioactive substance behaves almost exactly as being in solution. After the measurement had been finished, radioactivity can be removed from the liquid via filtration. In case of relatively long living radioisotopes the microcapsules can be reused.

As it was already mentioned, sometimes, it is advantageous and possible to remove microcapsules after use. Often, microcapsules can be reused. Nevertheless, in most cases the capsules must release the core substance into the liquid. Depending on the specific requirements of the system the release can be either controlled (slow) or "on command" (rapid).

Controlled release can be achieved as the result of:

- Biodegradation of the polymer (uniform distribution of the core in the polymer), dissolution of the polymer, decomposition of the polymer (under environment temperature, pressure, pH, etc.), and diffusion of the core substance through the polymeric wall.

Biodegradation, dissolution and decomposition of the polymer are applicable rather to microentrapment than to microencapsulation. Usually, the diffusion approach is the most convenient and, thus, the most common.

The mechanisms of "on command" release are numerous. They take advantage of various physical phenomena. The list of applicable types of the wall material include:

UV sensitive polymers, electron beam sensitive polymers, laser sensitive polymers, pH change sensitive polymers, ionic strength sensitive polymers, alpha, beta or gamma radiation sensitive polymers, magnetic field sensitive polymers, and heat (temperature change) sensitive polymers.

Additionally, the possible mechanism of "on command" rupture includes the use of ultrasound (with the frequency adjusted to the size of the capsules), microwave (with the capsules containing small amount of metal) and compressive force.

As it was already emphasized to successfully microencapsulate additives to liquid products it is essential to end up with the uniform distribution of capsules in the medium. Two factors must be taken into account: capsules density, and capsules size.

Usually, the encapsulated chemicals have higher density than the liquid they are in. Moreover, in case of petroleum products the density of the polymer (the wall material) is higher than the density of hydrocarbons mixture. It derives from the fact that even if monomers are hydrocarbons (aliphatic hydrocarbons exhibit lower density than other liquid compounds) the corresponding polymers will be of higher density than petroleum products (mixture of hydrocarbons). Therefore, it is necessary to be able to decrease the density of the capsule. It can be achieved by:

Introducing into the capsule an appropriate amount of compound, that produces gas (nitrogen, carbon dioxide, carbon monoxide, etc) under selected conditions.

The following compounds can serve as examples: ammonium carbonate, sodium hydrogen carbonate (salts capable of releasing carbon dioxide, azobisisobutyronite and similar azo compounds (compounds releasing nitrogen when heated), malonic acid and its analogs and derivatives including Meldrum acid, coumalic acid, acetonedicarboxylic acid, acetoacetic acid phenylacetoacetic acid and its analogs and derivatives including esters.

Using a wall material (polymer) which produces gas (i.e., carbon dioxide) under specific conditions (such as polymers of p-vinylbenzoylacetic acid). Microencapsulation carried at lower temperature than the working temperature (if capsules expand more than the core during the warm up). Microencapsulation carried at low temperature, in the presence of the natural gas such as argon (solubility of gases in the liquid decreases with the temperature increase). Introducing an appropriate amount of a liquid of low density (such as hexane or decane) into the capsule. Introducing gas into the capsule during microencapsulation. Also, adding a substance containing bubbles of gas (like Styrofoam) or hollow spheres (available for example from Polysciences) to the core during microencapsulation.

Sometimes, the average density of the capsules is lower than the liquid density. Then, the capsule density must be appropriately increased. It can be accomplished by implanting a substance of high density into the capsules. High density solids like some salts or high density liquids such as these containing halogens are probably the simplest potential remedies.

Another factor, which should be considered when trying to achieve the uniform distribution of the capsules in the liquid, is the size of the capsules. It is well known that Brownian motion can keep small, solid particles in such medium as the gas. However, it must be pointed out that there is certain optimum of the capsules size. On one hand the smaller the capsules the more uniform distribution of denser particles in the fluid medium. On the other hand the bigger

the microcapsules the larger the load (the amount of core substance per given amount of the wall material). At this point we think that the optimal size of microcapsules related to this invention is between 1 and 50 microns.

When choosing the wall forming polymers several factors and limitations must be taken into account. Here are some of the limitations one should consider. The polymeric wall material should be insoluble in the liquid capsules are in, insoluble in the core substance (if it is a liquid), and be neutral towards the core substance. Also, the wall material should be neutral towards the liquid components, and not adhere or react with pipelines, tanks, pumps, bottles, containers or any other material the liquid product may be in contact with.

Further, such material should be capable of forming products of required density, release the core substance only under the action of a selected triggering mechanism, and release the core substance rapidly when needed to enable the production of microcapsules of a specific diameter.

There are also factors to consider which are specific for given application. For example, in the case of microencapsulation of fuel additives additional limitations must not be forgotten.

The polymer should not contain hetero-elements such as silicon or halogens. Otherwise the combustion products will contain such undesirable compounds as silicon dioxide or halogen oxides. The polymer should form volatile products during combustion. However, in the case of so called flame or fuel additives, the microcapsule must rupture in the engine intake valve; thus, the rupture temperature must be precisely selected.

Often solid or liquid chemicals accompany certain liquids but there is a concern that these chemicals may interact with each other, with the liquid they are in or with the environment such as air, pipelines, pumps and other materials. In such cases there is a need to prevent the contact between a liquid or solid material and the liquid they are in. The effective method of preventing the contact between small amounts of gaseous, liquid or solid material and the high volume liquid is encapsulation. Microencapsulation is particularly useful.

However, it is usually important that the materials of interest are uniformly distributed in the high volume liquid such as petroleum products or water. When the compounds of interest are dissolved in the liquid they are by definition distributed uniformly. Unfortunately, as it was already pointed out the dissolution of these materials that are incompatible with each other or mixture components must be avoided. Simple microencapsulation causes that microcapsules either float on the surface of the liquid or end up at the bottom depending on the relative densities of capsules and the liquid they are in.

The object of this invention is a formation of micro(nano)capsules with controlled density to produce capsules exhibiting the same nominal density as the liquid they are in. Capsules exhibiting the same density as the liquid they are in are naturally uniformly distributed in the liquid i.e. any equal volume aliquot taken from the mixture will contain the same number of microcapsules.

Besides some exotic applications, the density of the liquid cannot be adjusted. Therefore, the only option to produce capsules exhibiting the same density as a liquid they are in is to adjust the density of capsules to the density of the liquid. The problem can be reduced to two opposite approaches determined by the relative densities of the capsules and the liquid.

If the formed capsules are of lower density than that of a liquid they are to be in, the capsules density must be appropriately increased. It can be accomplished by: (a) introducing a liquid of higher density into the microcapsule' core (payload), (b) introducing a solid of higher density into the microcapsule' core (payload), and (c) decreasing the capsules' volume after their formation.

More often the capsules' density is higher than the liquid's density and capsules density must be decreased. It can be achieved by: (a) introducing a liquid of lower density into the microcapsule' core (payload), (b) introducing a solid of lower density into the microcapsule' core (payload), and (c) increasing the capsules' volume or decreasing their mass after their formation.

Additionally, it is possible to influence the capsules density by using the wall material that is more or less dense than the core or by introducing a gas into microcapsules. These options, while applicable, do not seem to be practical. It is

particularly true for applications related to petroleum products, with usual densities being significantly below 1 g/cc.

It must be emphasized that substances that can be introduced into micro(nano)capsules must fulfill some requirements. For example, the capsules' wall material is usually permeable for small molecules. Thus, such molecules should not be employed as density altering agents because the capsules density would change with time due to a gradual disappearance (diffusion) of one of the core materials. Also, compounds altering density cannot react with the wall material, should not produce toxic decomposition products during capsules rupture et cetera.

Microcapsules' core material must often be released to the environment at certain point. There are many stimuli that can be applied for this purpose. They include: ultrasound of appropriate frequency; temperature increase (if microcapsules contain some compounds of appropriate boiling point, the increase of temperature above this boiling point causes tremendous pressure increase inside the capsule and eventual rupture); mechanical or osmotic pressure; pH or ionic strength change; and UV, laser or electron beam.

Additionally, it is conceivable to produce micro(nano)capsules with "intelligent" wall material that responds only to the presence of certain stimulus i.e. the core substance is released only if the stimulus of interest is present. For example, when the core material is a flame retardant and the stimulus causing the encapsulate release is the temperature increase caused by the fire.

There are possible numerous applications requiring uniform distribution of mixture components but such that these components are prevented from any contact with their environment until the required moment. For example, it is often of importance to know the capacity of a tank, barge or a reactor cooling system. Such capacities may change with time due to various factors such as corrosion. At present, the most frequently used method takes advantage of radioactivity (DIDA - direct isotope dilution analysis). However, many applicable radioactive compounds do not dissolve in the liquids of interest and may adhere to the walls

of the container. Additionally, methods taking advantage of radioactivity are not neutral to the personnel and cause tremendous problems with radioactive waste.

Certain number (X1) of microcapsules with the density equal to the density of the liquid filling the tank is added. After a brief stirring or mixing, the aliquot (volume = V2) is taken from the tank and the number of microcapsules in the aliquot is measured (X2). Capsules counter can be used for this purpose. Alternatively, capsules are filtered and counted or measured using an instrument taking advantage of the properties added to the surface or the core such as fluorescence. The capacity of the tank (V1) can be determined using the following equation: $V1 = V2 \times X1 / X2$.

Another potential application is related to marking of liquid products. Present art methods use taggants or markers that are dissolved. In many instances there is a legitimate concern that the dissolved markers can deteriorate in the liquid due to reactions between the markers and their environment.

Petroleum products are usually mixtures consisting of very many compounds, they are in contact with various environments (water, acids, free radicals. air, metals including steel, polymers et cetera), numerous chemicals are added to petroleum products as so called additives. That is why there is concern for markers of petroleum products including crude oils. Uniformly distributed microcapsules answer this concern. Their core material can contain an encryption to identify the liquid product. If needed, the microcapsules are ruptured and the encryption is read out to ensure the origin of the sample. A relevant quantitation is also possible. For example, the encapsulate (core) can contain certain amount of an appropriate color or fluorescent dye. During the measurement the capsules are ruptured to release the dye and its amount is quantified. Since the number of capsules and, hence, the quantity of the dye is proportional to the volume of a liquid dye quantitation enables to determine the volume of a (flowing) liquid.

The crucial issue is the micro(nano)capsules density. It must be adjusted to the density of the liquid petroleum product. The products of interest include but are not limited to: crude oils (densities 0.8 - 1.05); gasolines (densities about

0.86); diesel fuels (densities between 0.825 and 0.876), aviation fuels; individual refinery products such as hexane, cyclohexane, toluene et cetera; liquid fuels produced from gas; and liquid fuels produced from coal.

It must be emphasized that the densities shown are estimates and depend on amounts and types of additives such as ethyl alcohol (0.79). Furthermore, the use of microcapsules in marking is not limited to liquid hydrocarbon mixtures. Water based solutions and individual chemicals and solutions of various chemicals can be marked this way provided that the microcapsules are uniformly distributed in a liquid i.e. the densities of capsules and a liquid are equal. An important feature for some applications is that the capsules can be removed by filtration (if needed) before use.

Another aspect of the invention relates to the temperature changes. Density is temperature dependent and, usually, this dependence is little different for the liquid and the capsules. However, most of the products to be marked are not exposed to external temperatures. Also, in most cases the size of capsules is below 10 microns. This diameter should be as close as possible to the diameter at which the Brownian motion ensures uniform distribution. The diameter below which the Brownian motion is dominant depends on relative densities and other factors but for most applications is probably about 1 micron. In most instances, microcapsules cannot be that small. They have to carry some information. Moreover, the smaller they become the more material is used for the wall. In conclusion, it has to be said that it is beneficial to produce microcapsules exhibiting density as close as possible to that of a liquid and a diameter as close as practical to 1 micron. If these requirements are fulfilled the temperature related density changes are negligible for most applications.

Another potential application is related to microencapsulation of additives. Various liquids including hydrocarbon mixtures are treated with numerous additives which fulfill as diverse functions as corrosion inhibition, improvement of pouring properties of a liquid, removal of carbon deposits from the combustion chamber et cetera. Many of these additives are incompatible with each other, with mixture components or with materials and compounds, liquids

are in contacts with. Again, microencapsulation solves some of these problems. For example, carbon deposit removers can be microencapsulated together with a liquid exhibiting an appropriate boiling point. When the fuel approaches the engine the temperature rises causing that a liquid in the encapsulate tends to become vapor which leads to the capsules rupture and the release of the carbon deposits controlling agent. As before it is crucial that the capsules density is the same as the fuel density. Otherwise, the engine will be fed with fuel containing varying amounts of the additive.

Prior Art

There have not been any attempts to microencapsulate fuel additives. However, R. Rohde [U.S. Patent #4,066,559] patented a "container for oil-additive release", i.e. a polyolefin container or capsule containing additive to lubricant oil (such as oxidation inhibitor) which permeates through the container wall into the oil gradually. No attempt to adjust capsule density was made.

Microcapsules density is mentioned in a few patents. First, there is a very elegant method of tagging crude oils to detect the source of oil spills using encapsulated coded microspheres [U.S. Patent #3,964,294]. The authors propose to use microcapsules with density between 1.0 and 1.2, suitably 1.1 grams/mL so that the microspheroids will tend to collect at the interface of the oil slick and water. The disadvantage of the coding methodology is that it employs heteroatoms such as halogens and organometallic tags.

Second, Chang and Wiersema [U.S. Patent #4,708,816] propose a novel composition for treating fabrics. They prepare capsules with varying densities using the varying weight ratio of (ethylene derived hydrocarbon) polymer which forms the outer layer and coloring or whitening agents which forms the inner core. The purpose of changing the capsules density is to adjust to the varying densities of aqueous bleach solutions. One of the claims limits the density of the aqueous bleaching solutions to be about 1.08 g/mL and the outer layer of microcapsules has a density of about 0.91 to about 0.97 g/cc.

The existing methods of tagging (marking) hydrocarbon mixtures take advantage of compounds dissolved in the liquid product. The employed taggants

can belong to deuterated hydrocarbons, compounds that can be detected using appropriate antibodies (after the necessary sample manipulations) and various dyes including color and fluorescent dyes. A recent example of such tagging is discussed in an invention of M. Rutledge at al. [U.S. Patent #5,928,954]. The used taggants may exhibit excellent solubility in hydrocarbons, their detection and quantitation limits may be unsurpassed, the process economics may be very convincing. Nevertheless, based on their experience the present application authors believe that neither of these methods can withstand scrutiny in a court of law. The major problem with all such methods of tagging is that the taggants often stay in contact not only with a very complicated mixture of hydrocarbons (including unsaturated hydrocarbons) but also, plurality of additives, components of the pipeline system, pumps, tanks et cetera. Additionally, a contact with water, sunshine and air is usually unavoidable. Therefore, it is always conceivable that the taggants got deteriorated (decomposed) as a result of entering reactions with their environment. We strongly believe that tagging of such mixtures as petroleum mixtures unconditionally requires the use of micro(nano)capsules to prevent any contact of markers with petroleum products.

The most common and cost effective method of measuring the container's (such as a tank) capacity is (direct) isotope dilution analysis (DIDA) [Ehmann]. Similarly, radioactive tracers can be used for a leak detection and W.D. Ehmann, D.E. Vance, Radiochemistry and Nuclear Methods of Analysis, p. 313, in Chemical Analysis, Vol. 116, Ad. J.D. Winefordner, John Wiley & Sons, New York, 1991.

The following references are incorporated herein:

Raymond Rohde, Container for oil-additive release, U.S. Patent # 4,066,559; Jan. 3, 1978; Assignee: Phillips Petroleum Company. Michael J. Rutledge, Robert T. Roginski, George H. Vickers, Tagging Hydrocarbons for subsequent identification, U.S. Patent # 5,928,954; July 27, 1999;Assignee: BP Amoco Corporation. Frederick H. Shair, Peter G. Simmonds, Robert B. Leighton, Peter J. Drivas, Technique and system for coding and identifying

materials, U.S. Patent 3,964,294; June 22, 1976; Assignee: California Institute of Technology.

The design and structure of micro(nano)capsules with controlled density must fulfil certain conditions. First, they should be impermeable. Otherwise, the components of the encapsulate will diffuse from microcapsules which will gradually alter the capsules density. Therefore, gaseous substances or liquids consisting of small molecules should not be used as compounds decreasing the capsules density. However, recently Lambert et al. claim that elastic microspheres, filled with water insoluble gases, have been produced.

When solid beads such as hollow microspheres are used as the encapsulate components influencing the capsules density, the issue of permeability is much less important. In these cases the beads are relatively very huge objects and they cannot be released without the rupture of the capsules' wall.

Second, density is inversely proportional to the capsules volume but not to their diameter. It means that microcapsules that are to exhibit equal density should have the same volume, i.e. their size distribution should be perfectly uniform. Ideally uniform size distribution of microcapsules is practically impossible to achieve. When employing so called chemical methods of microcapsules' formation, the most narrow size distribution can be accomplished using microporous glass membrane such as Shirasu Porous Glass (SPG) emulsification technique [Ma, Omi, Muramatsu] during the formation of an appropriate emulsion. Spinning disc atomization [Hilborn] is probably the physical technique that produces the most narrow size distribution of microspheres. Recently, methods of formation of organic particles of controlled sizes were reviewed [Kumar].

Whichever method of microcapsules formation is used the size distribution will not be ideal. Therefore, some separation is necessary. The possible methods can take advantage either of the diameter of capsules or of their density [Ross]. Sieving is one of the methods that enables separation of microcapsules with the desired diameter (and thus, density) from all the produced

microcapsules. Alternatively, one can use hydrodynamic chromatography (HDC) to separate particles by their size.

The methods taking advantage of capsules density include gravitational sedimentation and (ultra)centrifugation. In sedimentation the produced capsules are suspended in the liquid exhibiting the appropriate density. Usually, it will be the one the capsules are to be introduced into. The capsules that float or sink are collected and removed from the system. The temperature of the separation can be adjusted.

Another potential option employs (ultra)centrifugation. The simplest case includes centrifugation in the liquid of interest. Particles (capsules) exhibiting neutral buoyancy (density equal to that of the liquid) are those that stay in the liquid. Additional methods may take advantage of continuous or non-continuous density gradient during (ultra)centrifugation. The use of gradient enables separation of produced microcapsules to fractions exhibiting desired density.

Every potential application of microcapsules with controlled density requires a decision whether it is more effective to produce capsules exhibiting very narrow size distribution and minimize separation or to put more emphasis on separation of the desired capsules from the mixture of capsules exhibiting broader size distribution. The answer is application specific. For example, microencapsulation of additives that are used in large quantities must be as ideal, if size distribution (and density) is concerned, as possible, to maximize the yield of microencapsulation. However, in the case of markers that are used in extremely small amounts, it can be cost effective to use more sophisticated methodology of capsules formation. This sophistication may be necessary to introduce an appropriate encryption into the capsules' core. It may mean that the capsules' size distribution was affected. Nevertheless, the cost of capsules is relatively low in this case and the unavoidable capsules separation may be a good option.

There are dozens of methods applicable to production of microcapsules. They are often divided to two groups: chemical and physical methods. Chemical methods are usually more robust and thus, more suitable for the formation of

micro(nano)capsules with controlled density. This statement by no means is intended to preclude the use of physical methods to produce microcapsules with controlled density. Two techniques are particularly applicable to production of microcapsules with controlled density (MCD). They are (simple and complex) coacervation and interfacial (condensation) polymerization.

Other references teaching a method for producing microcapsules include: J.G. Hilborn, Proceedings of 1994MRS Fall Meeting, 372, p. 63 (1994). D. Kumar, G.B. Butler, J.M.S.-Rev. Macromol. Chem. Phys., C37(2), 303 (1977). Karel J. Lambert, Sheila B. Podell, Edward G. Jablonski, Carl Hulle, Kenneth Hamilton, Rolf Lohrmann, Method for making encapsulated gas microspheres from heat denaturated protein in the absence of oxygen gas, U.S. Patent # 5,855,865; Jan. 5, 1999; Assignee: Molecular Biosystems, Inc. GH. Ma, M. Nagai, S. Omi, Colloids and Surfaces, A: Physiochemical and Engineering Aspects, 153, 383 (1999). N. Muramatsu, K. Shiga, T. Kondo, J. Microencapsulation, 11, 171 (1994). S. Omi, A. Matsuda, K. Imamura, M. Nagai, G-H. Ma, Colloids and Surfaces, A: Physiochemical and Engineering Aspects, 153, 373 (1999). S. Ross, I.D. Morrison, Colloidal Systems and Interfaces, J. Wiley & Sons, New York, 1988.

<u>Summary of Invention</u>

In one form of the invention, a method of making a liquid having a substantially uniform distribution of microcapsules, said microcapsules having a density adjusted to that of the liquid, which comprises the steps of determining the density of a liquid, adjusting the density of the microcapsules to approximate that of the density of the liquid and mixing the density adjusted microcapsules with the liquid. At least one compound or substance may be added to a payload of the microcapsule. The payload may have a density that is lower than the density of the microcapsules and includes a gas that may be produced inside of the payload.

Still another form of the invention includes structuring the microcapsule to release the payload in response to a triggering condition. The triggering

condition may include a reaction or a change in physical properties, either external or internal to the liquid.

Triggering conditions may include an energy source force such as an ultrasonic or ultraviolet laser, electron beam, magnetic field, microwave, radiant and radioactive energy sources applied to the microcapsule in the liquid.

One of the compounds utilized in the method for uniformly distributing a compound in a liquid includes an additive which is selected from a group of a corrosion inhibitor, a flame retardant and an antioxidant. Further, the additive may include a carbon deposit remover, a lead containing anti-knocking agent added to hydrocarbons, an agent for maintaining the hydrocarbon as a liquid or other agents.

The additive compound may also be a taggant for a petroleum product. Such taggant may be an agent which is capable of external detection, adding to an enclosed space a liquid having a substantial uniform distribution of microcapsules which contains a taggant, said microcapsules having a density adjusted to the density of the liquid and detecting whether the taggant has been admitted from said enclosed space.

Still another form of the invention includes a method for using a liquid having a substantial uniform distribution of microcapsules which contains a taggant, said microcapsules having a density adjusted to the density of the liquid comprising the steps of adding to an enclosed space a liquid having a substantial uniform distribution of microcapsules which contains a known amount of a taggant, said microcapsules having a density adjusted to the density of the liquid and removing at least a portion of said liquid containing the taggant from said enclosed space and determining the concentration of the taggant in said enclosed space.

Still another form of the invention is a method for determining the capacity of a tank using microcapsules that are uniformly distributed in a liquid, said microcapsules having a density adjusted to that of a liquid comprising the steps of adding a liquid to a tank, determining a density of a microcapsule and a density of the liquid, adjusting the density of microcapsule to within at least about

95% of the density of the liquid, adding a number of the adjusted density microcapsules to the liquid, mixing the liquid and the adjusted density microcapsules to form a substantially uniform mixture and removing volume of the mixture, counting a number of microcapsules in the removed volume, dividing said number of the density adjusted microcapsules added to the liquid by said number of the microcapsules in the removed volumes to yield a ratio and multiplying said volume and said ratio

whereby a capacity of the liquid added to the tank is calculated.

Brief Description of the Drawings

Fig. 1 is a diagram of the steps of a method of making a liquid having a substantially uniform distribution of microcapsules.

Detailed Description of Preferred Embodiments

The invention includes a method of making a liquid having a substantially uniform distribution of microcapsules. An illustration of the steps of the method of the invention is shown in Fig. 1. The density of the liquid must be determined. As used herein, the term "specific gravity" is intended to include and be interchangeable with the term density. Such density may be determined using known specific gravity techniques. For well characterized liquids, the density may be ascertained by standard chemical references or disclosed by the manufacturer of the liquid in its material safety data sheet. Also, the density microcapsules may be determined similarly.

The density of the microcapsule is adjusted to approximate the density of the liquid. It is intended that microcapsule density approximates the density of the liquid such that the microcapsules are capable of uniform distribution within the liquid. This is expected when the average density of the microcapsules are at least about 95 percent of the density of the liquid to which density is adjusted. Further, it is intended that there will be a distribution of microcapsule densities for which the average density is adjusted to the density of the liquid forming a uniform distribution of microcapsules.

A substance may be added to the core of the microcapsule to increase or decrease the density of the microcapsule. When one or more substances are

added to a microcapsule, these one or more substances may be referred to as a payload. Such payload may include an encapsulate compound or other substances that may be liquids, solids or gases. As shown in step 5, the payload added to the microcapsule may be a liquid, solid, gas or a mixture thereof. When it is desired to decrease the density of the microcapsule so that it approximates the density of the liquid, the average density of the payload should have a lower density than the density of the liquid. For example, if the payload is a mixture of a solid and/or liquid, such mixture should have a average density that is lower than the density of the liquid to which the microcapsule density is adjusted. Similarly, when it is desired to increase the density of the microcapsule, the density of the payload should be greater than the average density of the liquid to which density is adjusted. Again, the payload may be a solid, liquid, or possibly a gas.

In addition to adding a substance to the microcapsule, the density of the microcapsule may be adjusted by increasing or decreasing the volume of the microcapsule. The volume of the microcapsule may be adjusted by several methods, including modifying the thickness of the walls of the microcapsule. The wall of the microcapsule may be modified by adding a substance, including a polymer or other chemical, to wall surfaces of the microcapsule.

After adjusting the density of the microcapsule, such microcapsule is mixed with the liquid to form a mixture having a substantially uniform distribution of microcapsules have an average density that is approximate the density of the liquid.

The payload may also be capable of producing a gas. Such gas producing payload may include ammonium carbonate, sodium hydrogen carbonate, and other salts capable of releasing carbon dioxide; azobisisobutyronitriles, azo compounds, and other compounds capable of releasing nitrogen; organic compounds capable of releasing carbon dioxide such as malonic acid and analogs, Meldrum acid, coumalic acid, acetonedicarboxylic acid, acetoacetic acid, phenylacetoacetic acid, and including analogs or esters thereof.

The payload may also be reactive with the liquid. A reactive payload may be used to detect the presence or absence of one or more substances in the liquid and/or other microcapsules.

The microcapsule may be structured to release at least a portion of a payload in response to a triggering condition A triggering condition may be external or internal to the liquid. Or the triggering condition may be external or internal to the microcapsule. The triggering condition may be a reaction with a chemical, enzyme or microorganism. The reaction may be with another chemical, enzyme or microorganism or other entity that is added to the liquid or comes in contact with the liquid.

The triggering condition may be a change in a chemical or physical properties of the liquid. These change is properties may include change in temperature of the liquid, a change in osmotic pressure of the liquid, a change in pH of the liquid, a change in ionic strength of the liquid or a change in any other physical or chemical property of the liquid.

The triggering condition may also include a change in the external or internal force applied tot he liquid. This may include an application of a mechanical force, including a shearing force, or an application of external or internal pressure to the liquid.

The triggering condition may be the application of an external or internal energy source that includes ultrasonic, ultraviolet, laser, electron beam, magnetic field, microwave, radiant, and radioactive energies.

Another embodiment of the invention includes payloads of at least one of a corrosion inhibitor, a flame retardant or an antioxidant. Also, a payloads may include a carbon deposit remover, a lead containing anti-knocking agent added to hydrocarbons, an agent for maintaining the hydrocarbon as a liquid, an agent for increasing an octane rating of the hydrocarbon, an agent for improving the pouring properties of the hydrocarbon, a product that forms a complex with a solute and an agent for reducing environmental pollutants resulting from combustion of the hydrocarbon. In the case of products for reducing pollutants, such products include MTBE. Such payloads may be used in combination or

separately. Also, such payloads may be useful for any type liquid, and may be useful for applications directed towards hydrocarbons, petroleum products, fuels and/or non-hydrocarbons.

Other preferred payloads of this invention include products for human or animal consumption. These payloads may be used for providing a nutrient to the product, including vitamins, or a preservative for such products.

Another preferred embodiment of this invention is a liquid having substantially uniform distribution of microcapsules which include a taggant for a hydrocarbon, non-hydrocarbon or a petroleum product. Such taggants should be capable of external detection, including detecting a leak in a tank, pipeline, or other vessel. The taggant may also contain a dye or a mixture of dyes which will may assist in the detection of the taggant visually or with the aid of a device, including a colorimeter.

The taggant may also include an encryption that may be used to identify the liquid and/or the payload.

Still another preferred embodiment of this invention includes a method for using a liquid having a substantially uniform distribution of microcapsules which contains a taggant to determine the identity, source, and/or chemical, physical or other properties of such liquid. This method may comprise adding a such liquid to an enclosed space and detecting whether the taggant has been emitted from said enclosed space. The enclosed space may include a reaction vessel, a storage tank, a conduit, a truck, a rail car, a barge, a oil tanker, a ship, an underground storage tank or a fuel tank. Still another preferred embodiment of this invention includes a method for using a liquid having a substantially uniform distribution of microcapsules which contains a taggant to determine the amount and/or concentration of such liquid. This method may include adding to an enclosed space such liquid having substantially uniform distribution of density-adjusted microcapsules, removing at least a portion of said liquid containing the taggant from said enclosed space and determining the amount or concentration of the taggant.

The detecting may be made by means selected from a mass spectrometer, a radioactive counter, a colorimeter, a spectrometer, an ultrasound device, a flowsensor, and a particle counter. These embodiments may be used to detect the presence and/or the leakage of liquid having a substantially uniform distribution of a microcapsule having a taggant. Also, the amount, concentration, and identity of such taggant may be determined, including ascertaining the chemical, physical or nuclear properties of such taggant and/or liquid.

Yet still another embodiment of this invention includes a method for determining the capacity of a tank using density-adjusted microcapsules as described above. The method may comprise adding a liquid to a tank and determining a density of the liquid. Using the density of the liquid, the density of microcapsule is adjusted to that approximate of the density of the liquid, which may be within at least about 95% of the density of the liquid. A known number of the adjusted density microcapsules are added to the liquid are mixed to a substantially uniform mixture. A known volume or portion of the mixture is removed and the number of microcapsules in such known volume or portion is determined. The number of the density-adjusted microcapsules added to the liquid is divided by the number of such microcapsules removed in the known volume to obtain a number ratio. This ratio is then multiplying by the known volume or portion removed to determine the capacity of the tank.

The invention is further disclosed and described in a set of non-limiting illustrative examples set forth below.

EXAMPLE 1

A polymer solution is prepared by dissolving novolac resin and 10 - 20% AIBN in a 4/1 acetone/ethyl acetate mixture. A solids concentration is 5 - 10% (w/v). Dried polybead hollow microspheres (Polysciences, 1.00 micron) are spray-coated with the polymer solution by an air-spray unit. Sequential layers are applied when needed. The nominal density of microcapsules is below 0.85 g/cm^3. The microspheres can be immersed prior to use in a dye solution (ethyl acetate

solution for short period of time (for example 30 seconds). The resulting microcapsules are of little higher density but contain encapsulated dye.

EXAMPLE 2

Interfacial polycondensation polymerization. Water-in-oil emulsion is obtained by stirring (1200 rpm) 10 mL of aqueous solution of hexamethylendiamine (1M) and sodium bicarbonate (3M), methylene chloride-hexane (3:1) 100 mL of terephtaloyl chloride (0.1 M solution in methylene chloride) is added dropwise. The mixture is stirred for additional 2 hours. After addition of hexane microcapsules are separated by centrifugation and washed with various solvents as cyclohexane, ethanol and water. After drying at room temperature the microcapsules are gently heated to appropriate temperature and cooled.

EXAMPLE 3

Preparation of aminoplast microcapsules having Santasol oil (ex-Monsanto) as core fill.

Following the methods described in ref. GB 2073132 to Wiggins Teape. An aqueous solution was prepared comprising of 20 parts by weight of melamine formaldehyde resin (70% active polymer, manufactured by BIP) ,48 parts of a polyacrylic acid copolymer (20% active polymer) and 180 parts of water. The pH of the aqueous solution was adjusted to pH 4.0 with conc. formic acid. The resulting mixture was then stirred at ambient conditions to allow partial condensation of the melamine-formaldehyde resin until a cloudy solution was formed.

Next, 120 parts of Santasol 340 oil (complex mixture of partially hydrogenated terphenyl & quaterphenyls)) was added to the above aqueous solution and homogenised with a high shear laboratory mixer to form a oil in water emulsion.

The oil-in-water emulsion was then transferred to a stirring 700ml resin pot immersed in a water bath and warmed to 400C. The temperature was maintained at 400C for 20 hours to complete the wall formation reaction. The

capsule dispersion formed was cooled to room temperature and the pH adjusted to pH 8-9 with 46% caustic liquor.

EXAMPLE 4

Preparation of aminoplast microcapsules having Hexane as core as core fill.

The procedure described in Example 3 was repeated with the exception that hexane was encapsulated in place of the mineral oil.

EXAMPLE 5

Preparation of aminoplast microcapsules having Isopar G (ex- Exxon) as core fill.

The procedure described in Example 1 was repeated with the exception that an isoparaffin oil (Isopar G) was encapsulated in place of the Santosol oil.

EXAMPLE 6

Evaluation in different density oil mixtures.

The above Examples 3-5 produced microcapsules in the size range of 1-10 µm as measured on Mastersizer Microplus Ver2.18 from Malvern Instruments Ltd.,

The density of the aminoplast microcapsules was approximated using equations from US Patent No 4708816 to Clorox.

A series of mixtures of the solvents dichoroethane and Isopar G were prepared having densities ranging from 0.8 - 1.1. The density balancing was achieved using different mix ratios of a chlorinated solvent with a hydrocarbon solvent. The aqueous microcapsules suspension from Examples 3-6 above (2 parts) were added to 40 parts of the mixed solvents. The microcapsules were dispersed in the solvent mix using a vortex mixer with the aid of 1% of emulsifier (oil soluble non-ionic , anionic or cationic surfactant). The dispersions were then left to stand and visually monitored over a period of 1 week.

EXAMPLE 7

Preparation of polyamide shell microcapsules having water as core fill.

Following the methods described in ref. WO 9724179 to Allied Colloids Ltd.

An aqueous solution was prepared which consisted of 294 parts by weight of water and 4 parts diethylenetriamine buffered at pH 9.5.

Next, an oil phase was prepared comprising of 30 parts polymeric emulsion stabiliser and 136 parts hydrocarbon solvent. The aqueous solution was added to the oil phase, and homogenised by an aid of a high shear laboratory mixer thereby producing a water-in-oil emulsion.

A second oil phase was prepared consisting of 4 parts terephthaloyl chloride and 124 parts hydrocarbon solvent.

The terephthaloyl chloride solution was added to the water-in-oil emulsion over 3 minutes and the resulting capsule dispersion stirred for 30 minutes to complete the wall forming reaction.

EXAMPLE 8

Preparation of polyamide shell microcapsules having water as core fill.

Similar operations to Example 7 of the invention were carried out except that 8 parts of diethylenetriamine were used in the aqueous solution and 8 parts of terephthaloyl chloride and 255 parts hydrocarbon solvent in the second oil solution.

EXAMPLE 9

The above Examples 7-9 produce microcapsules with a size of between 2 - 50 μm as measured on Mastersizer Microplus Ver.2.18.

The capsules were tested in solvent mixtures of varying density between 0.8 and 1.4 (as in Example 6). Three solvents were used : hydrocarbon solvent = 0.8 , santasol oil = 1.0 and dichloroethane = 1.2. The solvents were pre-saturated with water . 40 parts of each mixture were placed in boiling tubes to this 2 parts of microcapsules suspension of examples 7-9 were added. The microcapsules were dispersed in the solvent mix using a vortex mixer. The mixtures were then left to stand and visually monitored over a 1 week period.

EXAMPLE 10

Example 8 was repeated with a mixed solvent system comprising of a density of 1.0.

This was prepared using a mix of hydrocarbon solvent and dichloroethane.

40 parts of each solvent mixture were placed in boiling tubes to this 2 parts of microcapsules were added. The microcapsules were dispersed in the solvent mix using a vortex mixer. The mixtures were then left to stand and visually monitored.

EXAMPLE 11

Polybead hollow microspheres (Polysciences, Inc., 0.40 microns, suspension in water, catalogue # 23567) were dried under vacuum using rotary evaporator. Additionally, they were treated with some toluene and evaporated to ensure dryness. 0.070 g of the dried microspheres were suspended in 3 mL of toluene and treated with traces (about 4 mg) of Brij 35 and 0.14 g of phtaloyl chloride (Aldrich). Next, deionized water (20 mL) was added to the mixture and it was stirred magnetically for about 10 minutes. Then, an excess of 1,6-hexanediamine (Aldrich, 0.256 g) was added to the reaction mixture. The stirring was continued for additional 30 minutes. The resulting mixture was centrifuged, separated from the liquid (at the bottom of a tube) washed with water and centrifuged again. The produced microcapsules are floating when dispersed in water, ethanol, acetone and hexane. Their average diameter is between 10 and 25 are as estimated by the microscope picture.

The foregoing description of preferred embodiments of the invention has been presented for purposes of illustration and description, and is not intended to be exhaustive or to limit the invention to the precise form disclosed. The description was selected to best explain the principles of the invention and their practical application to enable others skilled in the art to best utilize the invention in various embodiments and various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention not be limited by the specification, but be defined by the claims set forth below.

WHAT IS CLAIMED IS:

1. A method of making a liquid having a substantially uniform distribution of microcapsules comprising the steps of:

determining the density of a liquid;

adjusting the density of the microcapsules to approximate the density of the liquid; and

mixing the density-adjusted microcapsules with the liquid.

2. The method of claim 1 further comprising adding at least one additive, taggant, encapsulate, or substance to a payload of the microcapsules.

3. The method of claim 2 wherein the adding step includes a payload that has a density that is lower than the density of the microcapsules.

4. The method of claim 3 wherein the payload is selected from a liquid and a solid.

5. The method of claim 4 wherein the liquid or solid has low density.

6. The method of claim 1 wherein the density of the microcapsule is selected from a hollow microsphere and a foam bead.

7. The method of claim 2 wherein the adding step includes the payload that produces a gas in the microcapsules to lower the specific gravity of the microcapsule.

8. The method of claim 7 wherein the adding step includes the payload that produces the gas is selected from ammonium carbonate, sodium hydrogen carbonate, and other salts capable of releasing carbon dioxide; azobisisobutyronitriles, azo compounds, and other compounds capable of releasing nitrogen; organic compounds capable of releasing carbon dioxide such as malonic acid and analogs, meldrum acid, coumalic acid, acetonedicarboxylic acid, acetoacetic acid, phenylacetoacetic acid, and including analogs and esters thereof.

9. The method of claim 2 wherein the adding step includes the payload that has a density that is higher than the density of the liquid.

10. The method of claim 1 wherein the adjusting step includes increasing or decreasing microcapsule volume.

11. The method of claim 2 wherein the adding step includes the payload that is reactive with the liquid.

12. The method of claim 2 wherein the adding step includes structuring the microcapsule to release the payload in response to a triggering condition.

13. The method of claim 12 wherein the adding step includes the triggering condition selected from a reaction with a chemical, an enzyme and a microorganism.

14. The method of claim 12 wherein the adding step includes the triggering condition selected from a change in temperature of the liquid, a change in osmotic pressure of the liquid, a change in pH of the liquid, a change in ionic strength of the liquid and a change in a physical or chemical property of the liquid.

15. The method of claim 12 wherein the adding step includes the triggering condition selected from an application of a pressure and a force on the liquid.

16. The method of claim 12 wherein the adding step includes the triggering condition selected from an ultrasonic, ultraviolet, laser, electron beam, magnetic field, microwave, radiant, and radioactive energy source applied to microcapsules in the liquid or after they have been separated from the liquid.

17. The method of claim 2 wherein the payload is selected from a corrosion inhibitor, a flame retardant and an antioxidant.

18. The method of claim 2 wherein the payload is selected from the group of a carbon deposit remover, an anti-knocking agent, an agent for maintaining the hydrocarbon as a liquid, an agent for increasing an octane rating of the hydrocarbon, an agent for improving the pouring properties of the hydrocarbon, a product that forms a complex with a solute and an agent for reducing environmental pollutants resulting from combustion of the hydrocarbon.

19. The method of claim 18 wherein the agent for reducing environmental pollutants resulting from combustion of the hydrocarbon is methyl tertiary butyl ether.

20. The method of claim 2 wherein the payload in the adding step is a product for human or animal consumption selected from a vitamin, a preservative or a nutrient.

21. The method of claim 2 wherein the adding step includes the taggant for a hydrocarbon, a non-hydrocarbon, or a petroleum product.

22. The method of claim 21 wherein the adding step includes the taggant capable of external detection.

23. The method of claim 22 wherein the taggant is at least one dye, mixture of dyes or other encryption containing products or materials.

24. A method for using a liquid having a substantially uniform distribution of microcapsules which contains a taggant, said microcapsules having a density adjusted to the density of the liquid, comprising the steps of:

adding to an enclosed space a liquid having a substantially uniform distribution of microcapsules which contains a taggant, said microcapsules having a density adjusted to the density of the liquid; and

detecting whether the taggant has been emitted from said enclosed space.

25. A method for using a liquid having a substantially uniform distribution of microcapsules which contains a taggant, said microcapsules having a density adjusted to the density of the liquid, comprising the steps of:

adding to an enclosed space a liquid having a substantially uniform distribution of microcapsules which contains a known amount of taggant, said microcapsules having a density adjusted to the density of the liquid; and

removing at least a portion of said liquid containing the taggant from said enclosed space;

and

determining the concentration of the taggant in said enclosed space.

26. The method of claim 25 wherein the determining step includes determining the amount of the liquid removed by means selected from a mass spectrometer, a radioactive counter, a colorimeter, a spectrometer, an ultrasound device, a flowsensor, and a particle counter.

27. The method of claims 24 or 25 wherein the enclosed space of the adding step is selected from a pipeline, a reaction vessel, a storage tank, a conduit, a

truck, a rail car, a barge, a oil tanker, a ship, an underground storage tank and a fuel tank.

28. The method of claim 24 wherein the detecting step includes detecting an amount of the liquid emitted.

29. The method of claim 24 wherein the detecting step includes detecting the type of the liquid emitted.

30. The method of claims 1 or 2 further comprising the step of purifying the microcapsules using means selected from filtration, gravitational sedimentation and hydrodynamic chromatography.

31. A method for determining the capacity of a tank using microcapsules that are uniformly distributed in a liquid, said microcapsules having a density adjusted to that of a liquid, comprising the steps of:

adding a liquid to a tank;

determining a density of a microcapsules and a density of the liquid;

adjusting the density of the microcapsule to within at least about 95% of the density of the liquid;

adding a number of the adjusted density microcapsules to the liquid;

mixing the liquid and the adjusted density microcapsules to form a substantially uniform mixture; and

removing a volume of the mixture;

counting a number of microcapsules in the removed volume;

dividing said number of the density adjusted microcapsules added to the liquid by said number of the microcapsules in the removed volume to yield a ratio; and

multiplying said volume of the mixture removed and said ratio; and

whereby a capacity of the liquid added to the tank is calculated.

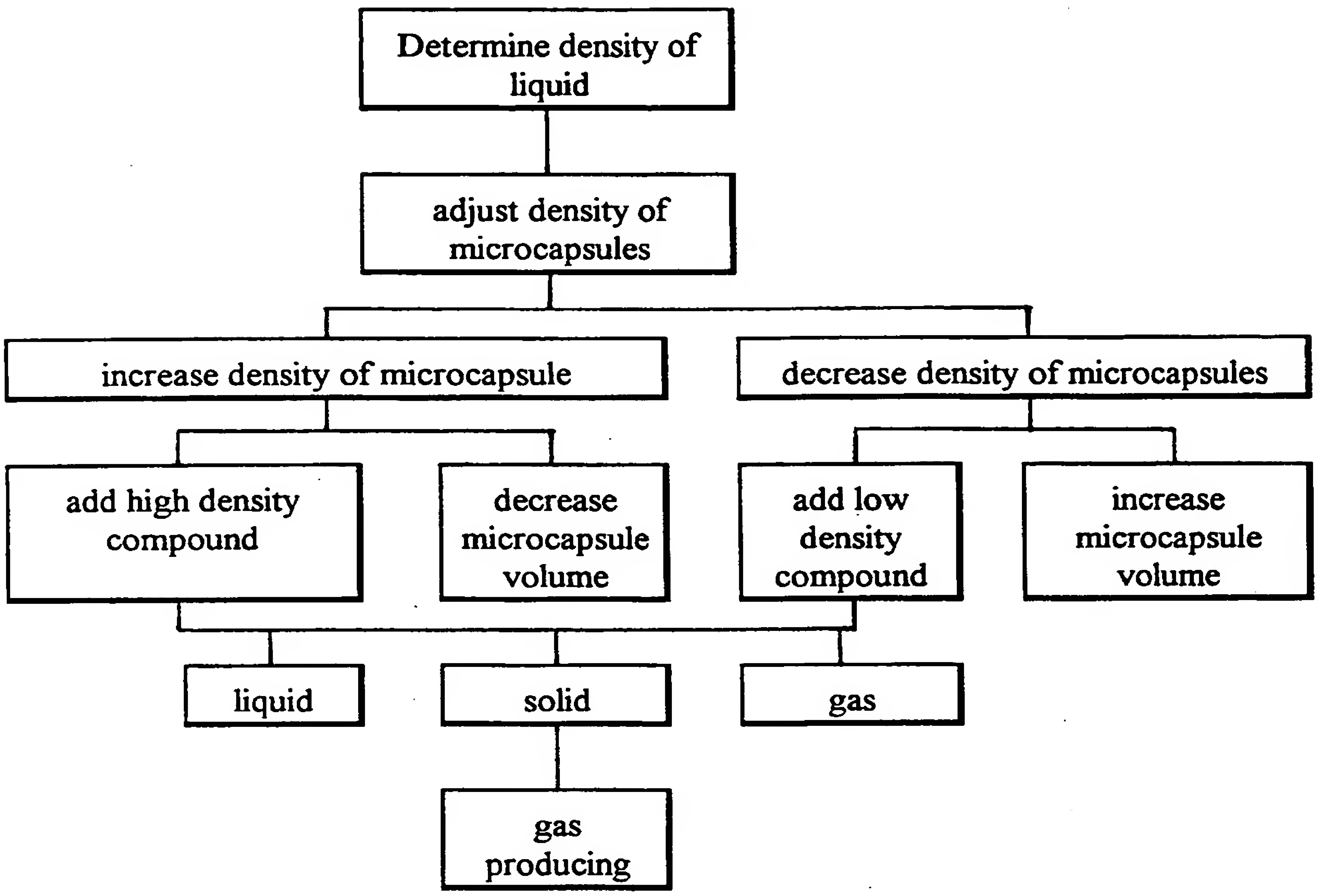
Determine density of liquid
adjust density of microcapsules
increase density of microcapsule
decrease density of microcapsules
add high density compound
decrease microcapsule volume
add low density compound
increase microcapsule volume
liquid
solid
gas
gas producing

Figure 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/09326

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :Please See Extra Sheet.
US CL :516/77; 44/502; 252/408.1; 264/4.3, 4.7; 436/56;73/861.41, 61.71
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 516/77; 44/502; 252/408.1, 965;264/4.3, 4.7; 436/56;507/907; 73/861.41, 61.71

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US 3,964,294 A (SHAIR et al) 22 June 1976, abstract; column 3, lines 3-16, column 7, line 28-column 10, line 8; and column 10, lines 58-65.	1-5, 9-11 and 20-30 — 6-8 and 12-19
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Y	US 2,797,201 A (VEATCH et al) 25 June 1957, Examples 1-4.	7, 8

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search	Date of mailing of the international search report
28 JULY 2000	17 AUG 2000

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	RICHARD D. LOVERING
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0651

INTERNATIONAL SEARCH REPORT

International application No.
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Form PCT/ISA/210 (continuation of second sheet) (July 1998)★

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER:
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(71) Applicant (*for all designated States except US*): PETRAMEC, INC. [US/US]; Ben Franklin Technology Center, 115 Research Drive, Jordan Hall, Bethlehem, PA 18015 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): BIELSKI, Roman [PL/US]; 1308 Sheridan Road, Coopersburg, PA 18036 (US). CARTER, John, E. [GB/US]; 411 Trails Court, Houston, TX 77024 (US).

(74) Agent: COOK, Tim; Bracewell & Patterson, L.L.P., 711 Louisiana Street, Suite 2900, Houston, TX 77002-2781 (US).

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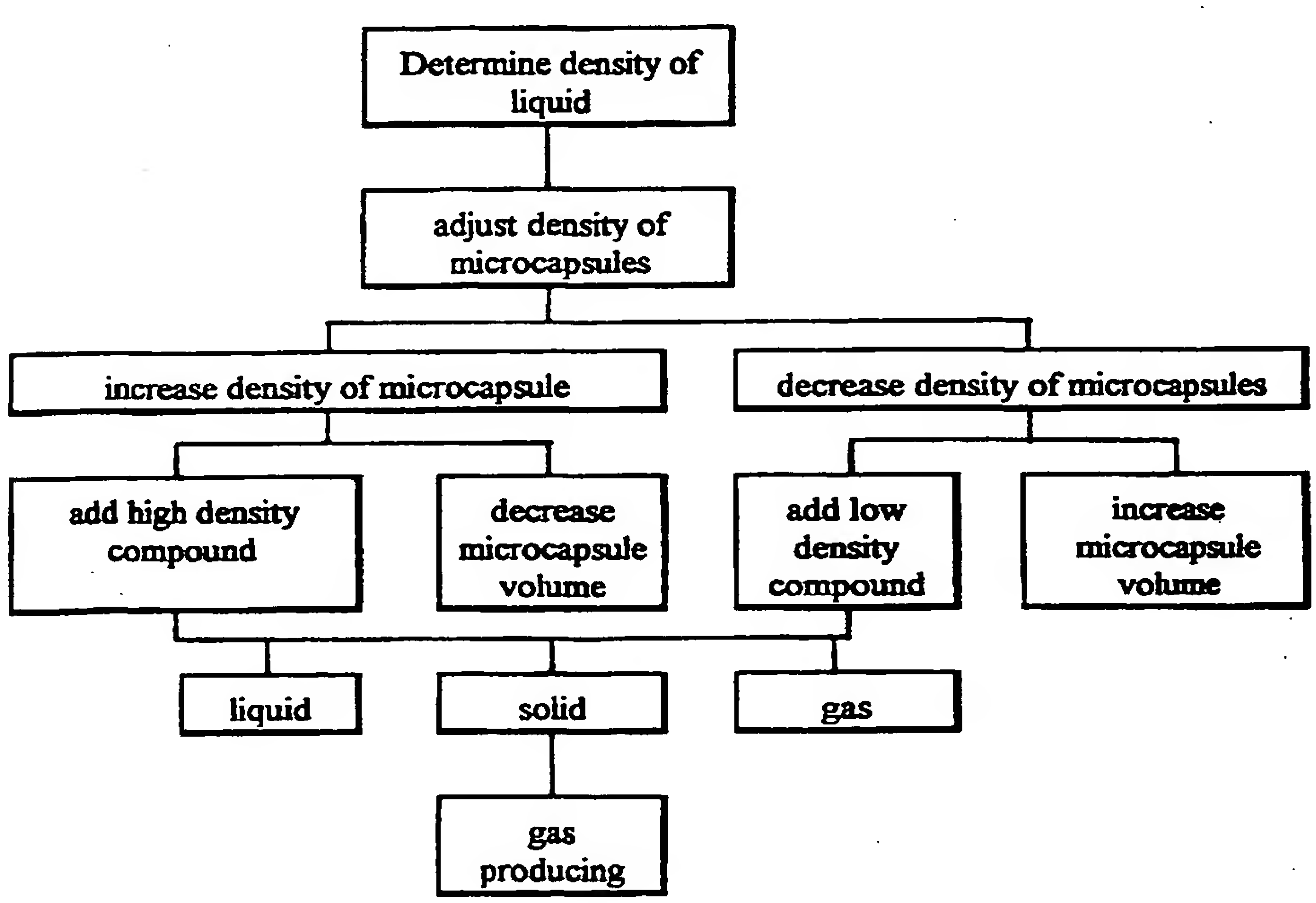
[Continued on next page]

(54) Title: METHODS OF MAKING AND USING MICROCAPSULES WITH CONTROLLED DENSITY



(57) Abstract: A method of making a liquid having a substantially uniform distribution of microcapsules having their density adjusted to approximate the density of a liquid. The microcapsules may be structured to encapsulate a payload including an additive that may be released upon a triggering condition as a marker which may be detected either externally or by internal. A method is taught that may be used to calculate the volume of a tank.

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International application No.
PCT/US00/09326

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US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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Date of the actual completion of the international search	Date of mailing of the international search report
28 JULY 2000	31 JAN 2001

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	D. L. Olekas for RICHARD D. LOVERING
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0651

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US CL :

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